

ON - LINE TEXT VALIDATION

17:37:03

ERROR REPORT

GROUP: T1

ISSUE DATE: 06/10/02

/PAGE NO: 2	LINE NO: 12	ERROR => NO SECTION COMMAND FOUND AT START OF TEXT
/PAGE NO: 2	LINE NO: 24	WARNING => MISSING LIGHT COMMAND (+1) FOLLOWING (+b) AFTER 50 !!
/PAGE NO: 11	LINE NO: 227	WARNING => INFER/SUPR COMMANDS MUST RETURN TO LIGHT AFTER 10
/PAGE NO: 11	LINE NO: 227	WARNING => INFER/SUPR COMMANDS MUST RETURN TO LIGHT AFTER 10

D A C S - E R R O R R E P O R T

PATENT #: 56055692.001

ISSUE DATE: 06/10/02

GROUP: T1

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INFO, NO DACS VALIDATION ERRORS HAVE BEEN FOUND...

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ENDED TEXT DACS VALIDATION FOR: ***** 56055692.001 *****

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--* NEW PATENT *-*-*

Group T1

PATENT # 56055692.001

0001 +pg,1

0002 +sa

0003 An ethylene/+60 -olefin polymer blend is described comprising first <<<<
>>>>and second ethylene/+60 -olefin

0004 polymer components in which the ethylene content of the first <<<<
>>>>component is at least 10

0005 weight percent different than the ethylene content of the second <<<<
>>>>component. These blends

0006 exhibit an improved combination of low temperature, pellet flow, <<<<
>>>>compression set, melt strength

0007 and/or shape retention properties as compared to either component, or <<<<
>>>>an ethylene/+60 -olefin

0008 polymer blend of similar composition but in which the ethylene <<<<
>>>>content of each component is

0009 substantially the same.

0010 +ea

0011 +pg,2

0012 +p This application claims priority from Provisional application Ser. <<<<
>>>>No. +b 60/203,298, +1

0013 filed May. +b 11, 200⁰₁.

0014 +su +cl FIELD OF THE INVENTION

0015 +p This invention relates to ethylene/+60 -olefin polymer blends. In <<<<
>>>>one aspect, this invention

0016 relates to polymer blends comprising two or more ethylene/+60 -olefin <<<<
>>>>components while in

0017 another aspect, this invention relates to blends in which one or more <<<<
>>>>of the components

0018 comprises an ethylene/+60 -olefin/polyene polymer. In yet another <<<<
>>>>aspect, this invention relates to

0019 polymer blends of ethylene/+60 -olefin components in which the <<<<
>>>>ethylene content of one

0020 component differs from the ethylene content of at least one other <<<<
>>>>component by at least about +b 10 +1

0021 weight percent.

0022 +cl BACKGROUND OF THE INVENTION

0023 +p Ethylene/+60 -olefin polymer blends are well known in the art. The <<<<
>>>>blends taught in U.S. Pat₀ Nos.

0024 +b 4,438,238; 4,722,971; 4,874,820; 4,902,738; 4,937,299; 4,939,217; <<<<
>>>>5,013,801; 5,236,998;

0025 5,292,845; 5,382,631; 5,494,965; 5,539,076; 5,691,413; 5,728,766; 4,<<<<
>>>>429,079; 4,530,914;

0026 5,605,969; 5,338,589; 5,260,384; 5,478,890; 5,438,100; 5,476,903; 5,<<<<
>>>>703,180; 5,464,905;

0027 5,744,551; 5,747,620 +1 and +b 5,798,427 +1 are representative, and <<<<
>>>>each of these patents are

0028 incorporated herein by reference.

0029 +p Blends are useful because they provide properties not available <<<<
>>>>from the individual

0030 components from which the blend is made. For example, an ethylene/+60 <<<<
>>>>-olefin polymer with a

0031 relatively narrow molecular weight distribution (MWD), e.g., +b 2 +l <<<<
>>>>or less, will usually produce a

0032 film with good transparency but it will usually process less <<<<
>>>>efficiently than an ethylene/+60 -olefin

0033 +pg,3

0034 polymer alike in all aspects except with a MWD of +b 3 +1 or more. <<<<
>>>>However, an ethylene/+60 -olefin

0035 polymer with a MWD of +b 3 +1 or more usually produces a film that is <<<<
>>>>less transparent than a like

0036 ethylene/+60 -olefin polymer with a MWD of +b 2 +1 or less. Blending <<<<
>>>>the two polymers will usually

0037 produce a composition that will produce a film with both desirable <<<<
>>>>transparency and

0038 processability. Moreover, depending upon the particular ethylene/+60 -<<<<
>>>>olefin polymers, the relative

0039 proportions of each, the manner in which the polymers are made and/or <<<<
>>>>blended, the properties

0040 of interest and a host of other variables, one or more properties of <<<<
>>>>the blend may be more than a

0041 simple average of its component parts.

0042 +p While ethylene/+60 -olefin polymer blends can be prepared by any <<<<
>>>>one of a number of

0043 different processes, generally these processes fall into one of two <<<<
>>>>categories, i.e., post-reactor

0044 blending and in-reactor blending. Illustrative of the former are melt <<<<
>>>>extruders into which two or

0045 more solid ethylene/+60 -olefin polymers are fed and physically mixed <<<<
>>>>into a substantially

0046 homogeneous composition, and multiple solution, slurry or gas-phase <<<<
>>>>reactors arranged in a

0047 parallel array the output from each blended with one another to form <<<<
>>>>a substantially

0048 homogeneous composition which is ultimately recovered in solid form. <<<<

>>>>Illustrative of the latter

0049 are multiple reactors connected in series, and single reactors <<<<
>>>>charged with two or more catalysts.

0050 While each general process category has its own advantages and <<<<
>>>>disadvantages, in-reactor

0051 blending is a favored technique for making blends in which component <<<<
>>>>compatibility, i.e., the

0052 ability to make a substantially homogeneous blend from the components,<<<<
>>>> is a factor. Generally,

0053 forming a substantially homogeneous blend from ethylene/+60 -olefin <<<<
>>>>polymer components that are

0054 less than fully compatible is easier and more successful and cost <<<<
>>>>effective using an in-reactor

0055 technique than a post-reactor technique, particularly melt extrusion.

0056 +pg,4

0057 +p Ethylene/+60 -olefin polymers and blends of these materials are <<<<
>>>>commercially important

0058 because they exhibit and/or impart desirable properties to various <<<<
>>>>products, e.g., films and

0059 molded and extruded articles. Properties of frequent interest are low <<<<
>>>>temperature impact

0060 strength, compression set, melt strength, shape retention, pellet <<<<
>>>>flow, mechanical strengths and

0061 modulus. Depending upon the end use, often one or more of these <<<<
>>>>properties will be more

0062 important than the others. Enhancement of these more important <<<<
>>>>properties often requires the

0063 use of a blend of ethylene/+60 -olefin polymers. The industry <<<<
>>>>interest, of course, is in blends in

0064 which the properties of primary importance are enhanced without <<<<
>>>>significant diminution of the

0065 other properties.

0066 +cl SUMMARY OF THE INVENTION

0067 +p According to this invention, ethylene/+60 -olefin polymer blends <<<<
>>>>with improved low

0068 temperature, pellet flow, compression set, melt strength and/or shape <<<<
>>>>retention properties are

0069 prepared by blending a first ethylene/+60 -olefin polymer component <<<<
>>>>with a second ethylene/+60 -olefin

0070 polymer component, with the proviso that the ethylene content of the <<<<
>>>>first and second

0071 ethylene/+60 -olefin polymer components differ from one another by at <<<<
>>>>least about +b 10 +l weight

0072 percent. The blends can be made by either post-reactor or in-reactor <<<<
>>>>blending, and the weight

0073 ratio of first component to second component can vary widely, <<<<
>>>>typically from between +b 80:20 +1 to

0074 +b 20:80. +1 One hallmark of this invention is that the enhanced <<<<
>>>>properties of the blend are achieved

0075 without significant diminution of other desirable properties of the <<<<
>>>>blend components.

0076 +pg,5

0077 +dr +cl BRIEF DESCRIPTION OF THE DRAWINGS

0078 +p FIG. 1 is a graph reporting the residual crystallinity of <<<<
>>>>exemplary elastomer blends of

0079 this invention as compared to a control elastomer.

0080 +p FIG. 2 is a graph reporting the modulus G+40 +0 of exemplary <<<<
>>>>elastomer blends of this

0081 invention as compared to a control elastomer and two commercially <<<<
>>>>available elastomers.

0082 +de +cl DETAILED DESCRIPTION OF THE INVENTION

0083 +p The ethylene/+60 -olefin blend components of this invention are <<<<
>>>>polymers, i.e.,

0084 interpolymers, of ethylene with at least one C+hd 3+1 ^{+14A} C+hd 20 +1 +60 <<<<
>>>>-olefin (preferably an aliphatic +60 -olefin)

0085 comonomer, and/or a polyene comonomer, e.g., a conjugated diene, a <<<<
>>>>nonconjugated diene, a

0086 triene, etc. The term interpolymers includes copolymers, e.g. <<<<
>>>>ethylene/propylene (EP), and

0087 terpolymers, e.g. EPDM, but it is not limited to polymers made with <<<<
>>>>only ethylene and one or

0088 two monomers. Examples of the C+hd 3+1 ^{+14A} -C+hd 20 +1 +60 -olefins <<<<
>>>>include propene, +b 1+1 -butene, +b 4+1 -methyl-+b 1+1 -pentene,

0089 +b 1+1 -hexene, +b 1+1 -octene, +b 1+1 -decene, +b 1+1 -dodecene, +b <<<<
>>>>1+1 -tetradecene, +b 1+1 -hexadecene, +b 1+1 -octadecene

0090 and +b 1+1 -eicosene. The +60 -olefin can also contain a cyclic <<<<
>>>>structure such as cyclohexane or

0091 cyclopentane, resulting in an +60 -olefin such as +b 3+1 -cyclohexyl-<<<<
>>>>+b 1+1 -propene (allyl-cyclohexane) and

0092 vinyl-cyclohexane. Although not +60 -olefins in the classical sense <<<<

>>>>of the term, for purposes of this

0093 invention certain cyclic olefins, such as norbornene and related <<<<
>>>>olefins, are +60 -olefins and can be

0094 used in place of some or all of the +60 -olefins described above. <<<<
>>>>Similarly, styrene and its related

0095 olefins (e.g., +60 -methylstyrene, etc.) are +60 -olefins for <<<<
>>>>purposes of this invention.

0096 +pg,6

0097 +p Polyenes are unsaturated aliphatic or alicyclic compounds <<<<
>>>>containing more than four

0098 carbon atoms in a molecular chain and having at least two double <<<<
>>>>and/or triple bonds, e.g.,

0099 conjugated and nonconjugated dienes and trienes. Examples of <<<<
>>>>nonconjugated dienes include

0100 aliphatic dienes such as +b 1,4+1 -pentadiene, +b 1,4+1 -hexadiene, <<<<
>>>>+b 1,5+1 -hexadiene, +b 2+1 -methyl-+b 1,5+1 -hexadiene,

0101 +b 1,6+1 -heptadiene, +b 6+1 -methyl-+b 1,5+1 -heptadiene, +b 1,6+1 -<<<<
>>>>octadiene, +b 1,7+1 -octadiene, +b 7+1 -methyl-+b 1,6+1 -octadiene,

0102 +b 1,13+1 -tetradecadiene, +b 1,19+1 -eicosadiene, and the like; <<<<
>>>>cyclic dienes such as +b 1,4+1 -cyclohexadiene,

0103 bicyclo+8 +b 2.2.1+1 +9 hept-+b 2,5+1 -diene, +b 5+1 -ethylidene-+b <<<<
>>>>2+1 -norbornene, +b 5+1 -methylene-+b 2+1 -norbornene, +b 5+1 -vinyl-+b <<<<
>>>>

0104 2+1 -norbornene,

0105 bicyclo+8 +b 2.2.2+1 +9 oct-+b 2,5+1 -diene, +b 4+1 -vinylcyclohex-+b <<<<
>>>>1+1 -ene, bicyclo+8 +b 2.2.2+1 +9 oct-+b 2,6+1 -diene,

0106 +b 1,7,7+1 -trimethylbicyclo-+8 +b 2.2.1+1 +9 hept-+b 2,5+1 -diene, <<<<
>>>>dicyclopentadiene, methyltetrahydroindene, +b 5+1 -allylbicyclo+8

0107 +b 2.2.1+1 +9 hept-+b 2+1 -ene, +b 1,5+1 -cyclooctadiene, and the <<<<
>>>>like; aromatic dienes such as +b 1,4+1 -diallylbenzene,

0108 +b 4+1 -allyl-+b 1+1 H-indene; and trienes such as +b 2,3+1 -<<<<
>>>>diisopropenylidene-+b 5+1 -norbornene, +b 2+1 -ethylidene-+b

0109 3+1 -isopropylidene-+b 5+1 -norbornene, +b 2+1 -propenyl-+b 2,5+1 -<<<<
>>>>norbornadiene, +b 1,3,7+1 -octatriene,

0110 +b 1,4,9+1 -decatriene, and the like; with +b 5+1 -ethylidene-+b 2+1 -<<<<
>>>>norbornene, +b 5+1 -vinyl-+b 2+1 -norbornene and +b 7+1 -methyl-+b

0111 1,6+1 -octadiene preferred nonconjugated dienes.

0112 +p Examples of conjugated dienes include butadiene, isoprene, +b 2,<<<<
>>>>3+1 -dimethylbutadiene-+b 1,3,1,2+1 -dimethylbutadiene-+b 1,3,1,4+1 -<<<<
>>>>dimethylbutadiene-+b 1,3,1+1 -ethylbutadiene-+b 1,3,2+1 -<<<<
>>>>phenylbutadiene-+b 1,3, +1 hexadiene-+b 1,3,4+1 -methylpentadiene-+b 1,<<<<
>>>>3,1,3+1 -pentadiene (CH+hd 3+1 CH+50 CH+13 CH+50 CH+hd 2+1 ; commonly

0113 called piperylene), +b 3+1 -methyl-+b 1,3+1 -pentadiene, +b 2,4+1 -<<<<
>>>>dimethyl-+b 1,3+1 -pentadiene, +b 3+1 -ethyl-+b 1,3+1 -pentadiene,

0114 and the like; with +b 1,3+1 -pentadiene a preferred conjugated diene.

0115 +p Examples of trienes include +b 1,3,5+1 -hexatriene, +b 2+1 -methyl-<<<<
>>>>+b 1,3,5+1 -hexatriene, +b 1,3,6+1 -heptatriene,

0116 +b 1,3,6+1 -cycloheptatriene, +b 5+1 -methyl-+b 1,3,6+1 -heptatriene, <<<<
>>>>+b 5+1 -methyl-+b 1,4,6+1 -heptatriene,

0117 +b 1,3,5+1 -octatriene, +b 1,3,7+1 -octatriene, +b 1,5,7+1 -<<<<
>>>>octatriene, +b 1,4,6+1 -octatriene, +b 5+1 -methyl-+b 1,5,7+1 -<<<<
>>>>octatriene,

0118 +b 6+1 -methyl-+b

0119 1,5,7+1 -octatriene, +b 7+1 -methyl-+b 1,5,7+1 -octatriene, +b 1,4,<<<<
>>>>9+1 -decatriene and +b 1,5,9+1 -cyclodecatriene.

0120 +pg, 7

0121 +p Exemplary copolymers include ethylene/propylene, ethylene/butene, <<<<
>>>>ethylene/+b 1+1 -octene,

0122 ethylene/+b 5+1 -ethylidene-+b 2+1 -norbornene, ethylene/+b 5+1 -<<<<
>>>>vinyl-+b 2+1 -norbornene, ethylene/-+b 1,7+1 -octadiene,

0123 ethylene/+b 7+1 -methyl-+b 1,6+1 -octadiene and ethylene/+b 1,3,5+1 -<<<<
>>>>hexatriene. Exemplary terpolymers include

0124 ethylene/propylene/+b 1+1 -octene, ethylene/butene/+b 1+1 -octene, <<<<
>>>>ethylene/propylene/+b 5+1 -ethylidene-+b 2+1 -norbornene,

0125 ethylene/butene/+b 5+1 -ethylidene-+b 2+1 -norbornene, ethylene/buten<<<<
>>>>e/styrene, ethylene/+b 1+1 -octene/+b

0126 5+1 -ethylidene-+b 2+1 -norbornene, ethylene/propylene/+b 1,3+1 -<<<<
>>>>pentadiene, ethylene/propylene/+b 7+1 -methyl-+b

0127 1,6+1 -octadiene, ethylene/butene/+b 7+1 -methyl-+b 1,6+1 -octadiene, <<<<
>>>>ethylene/+b 1+1 -octene/+b 1,3+1 -pentadiene

0128 and ethylene/propylene/+b 1,3,5+1 -hexatriene. Exemplary tetrapolymer<<<<
>>>>s include

0129 ethylene/propylene/+b 1+1 -octene/diene (e.g. ENB), ethylene/butene/+<<<<
>>>>b 1+1 -octene/diene and

0130 ethylene/propylene/mixed dienes, e.g. ethylene/propylene/+b 5+1 -<<<<
>>>>ethylidene-+b 2+1 -norbornene/piperylene.

0131 In addition, the blend components can include minor amounts, e.g. +b <<<<
>>>>0.05⁺⁴⁰~~+1~~-+b 0.5 +1 percent by weight,

0132 of long chain branch enhancers, such as +b 2,5+1 -norbornadiene (aka <<<<
>>>>bicyclo+8 +b 2,2,1+1 +9 hepta-+b 2,5+1 -diene),

0133 ^{as} diallylbenzene, +b 1,7+1 -octadiene (H+hd 2+1 C+50 CH(CH+hd 2+1 <<<<
>>>>)+hd 4+1 CH+50 CH+hd 2+1), and +b 1,9+1 -decadiene

0134 (H+hd 2+1 C+50 CH(CH+hd 2+1)+hd 6+1 CH+50 CH+hd 2+1).

0135 +p Typically, the blend components of this invention comprise at <<<<

>>>>least about +b 20, +l preferably

0136 at least about +b 30 +l and more preferably at least about +b 40, +l <<<<

>>>>weight percent ethylene; at least about +b 1, +l

0137 preferably at least about +b 5 +l and more preferably at least about <<<<

>>>>+b 10, +l weight percent of at least one +60 -olefin;

0138 and, if a polyene-containing terpolymer, greater than +b 0, +l <<<<

>>>>preferably at least about +b 0.1 +l and

0139 more preferably at least about +b 0.5, +l weight percent of at least <<<<

>>>>one conjugated or nonconjugated

0140 polyene. As a general maximum, the blend components of this invention <<<<

>>>>comprise not more

0141 than about +b 95, +l preferably not more than about +b 85 +l and more <<<<

>>>>preferably not more than about +b 75, +l

0142 weight percent ethylene; not more than about +b 80, +l preferably not <<<<

>>>>more than about +b 70 +l and more

0143 +pg, 8

0144 preferably not more than about +b 60, +l weight percent of at least <<<<
>>>>one +60 -olefin; and, if a terpolymer,

0145 not more than about +b 20, +l preferably not more than about +b 15 +l <<<<
>>>>and more preferably not more than

0146 about +b 12, +l weight percent of at least one of a conjugated or <<<<
>>>>nonconjugated diene. All weight

0147 percentages are based on weight of the blend.

0148 +p Important to this invention is that the difference in ethylene <<<<
>>>>content between the first and

0149 second components of the blend is at least about +b 10 +l weight <<<<
>>>>percent, preferably at least about +b 15 +l

0150 and more preferably at least about +b 20, +l weight percent. The <<<<
>>>>maximum difference in ethylene

0151 content between the first and second components of the blend can vary <<<<
>>>>widely although as a

0152 practical matter, the maximum difference does not exceed about +b 30, <<<<
>>>>+l preferably about +b 25, +l weight

0153 percent.

0154 +p The ethylene/+60 -olefin polymer components of this invention can <<<<
>>>>be produced using

0155 conventional ethylene/+60 -olefin polymerization technology. <<<<
>>>>Preferably, the ethylene/+60 -olefin

0156 polymer components of this invention are made using a mono- or bis-<<<<
>>>>cyclopentadienyl, indenyl,

0157 or fluorenyl transition metal (preferably Group +b 4+l) catalysts or <<<<
>>>>constrained geometry catalysts

0158 (CGC) in combination with an activator, in a solution, slurry, or gas <<<<
>>>>phase polymerization

0159 process. The catalyst is preferably mono-cyclopentadienyl, mono-
>>>>indenyl or mono-fluorenyl

0160 CGCs. The solution process is preferred. U.S. Pat. No. +b 5,064,802; <<<<
>>>>+l WO+b 93/19104 +l (U.S. Ser. No. +b 8,003, +l filed

0161 Jan. +b 21, 1993+l), and WO+b 95/00526 +l disclose constrained <<<<
>>>>geometry metal complexes and

0162 methods for their preparation. Variously substituted indenyl <<<<
>>>>containing metal complexes are

0163 taught in WO+b 95/14024 +l and WO+b 98/49212. +l The relevant <<<<
>>>>teachings of all of the foregoing patents

0164 or their corresponding U.S. patents or allowed applications are <<<<
>>>>hereby incorporated by reference

0165 for purposes of U.S. patent practice.

0166 +pg, 9

0167 +p In general, polymerization may be accomplished at conditions well <<<<
>>>>known in the art for

0168 Ziegler-Natta or Kaminsky-Sinn type polymerization reactions, that is, <<<<
>>>> temperatures from +b 0⁺¹ ~~-+b~~

0169 250⁺¹ +20 +0 C., preferably +b 30⁺¹ -+b 200⁺¹ +20 +0 C., and <<<<
>>>>pressures from atmospheric to +b 10,000 +1 atmospheres (+b 10¹³ +1

0170 megapascals (MPa)). Suspension, solution, slurry, gas phase, solid <<<<
>>>>state powder polymerization

0171 or other process conditions may be employed if desired. A support, <<<<
>>>>especially silica, alumina, or

0172 a polymer (especially poly(tetrafluoroethylene) or a polyolefin) may <<<<
>>>>be employed, and desirably

0173 is employed when the catalyst is used in a gas phase polymerization <<<<
>>>>process. The support is

0174 preferably employed in an amount sufficient to provide a weight ratio <<<<
>>>>of catalyst (based on

0175 metal):support within a range of from +b 1:100,000 +1 to +b 1:10, +1 <<<<
>>>>more preferably from +b 1:50,000 +1 to +b 1:20, +1

0176 and most preferably from +b 1:10,000 +1 to +b 1:30. +1 In most <<<<
>>>>polymerization reactions, the molar ratio of

0177 catalyst:polymerizable compounds employed is from +b 10+hu^{+31b} 12+b :1 +1 <<<<
>>>>to +b 10+hu^{+31p} 1+b :1, +1 more preferably from +b 10+hu +31

0178 9+b :1 +1 to +b 10+hu^{+31p} 5+b :1.

0179 +p Inert liquids serve as suitable solvents for polymerization. <<<<
>>>>Examples include straight and

0180 branched-chain hydrocarbons such as isobutane, butane, pentane, <<<<
>>>>hexane, heptane, octane, and

0181 mixtures thereof; cyclic and alicyclic hydrocarbons such as <<<<

>>>>cyclohexane, cycloheptane,

0182 methylcyclohexane, methylcycloheptane, and mixtures thereof; <<<<

>>>>perfluorinated hydrocarbons

0183 such as perfluorinated C₄-10 alkanes; and aromatic and alkyl-<<<<

>>>>substituted aromatic compounds

0184 such as benzene, toluene, xylene, and ethylbenzene. Suitable solvents <<<<

>>>>also include liquid olefins

0185 that may act as monomers or comonomers including butadiene, <<<<

>>>>cyclopentene, +b 1+1 -hexene, +b 1+1 -hexane,

0186 +b 4+1 -vinylcyclohexene, vinylcyclohexane, +b 3+1 -methyl-+b 1+1 -<<<<

>>>>pentene, +b 4+1 -methyl-+b 1+1 -pentene, +b 1,4+1 -hexadiene,

0187 +b 1+1 -octene, +b 1+1 -decene, styrene, divinylbenzene, allylbenzene,<<<<

>>>> and vinyltoluene

0188 (including all isomers alone or in admixture). Mixtures of the <<<<

>>>>foregoing are also suitable. If

0189 +pg,10

0190 desired, normally gaseous olefins can be converted to liquids by <<<<
>>>>application of pressure and used

0191 herein.

0192 +p The ethylene/+60 -olefin polymer components of this invention can <<<<
>>>>be blended by any in-reactor

0193 or post-reactor process. The in-reactor blending processes are <<<<
>>>>preferred to the post-reactor

0194 blending processes, and the processes using multiple reactors <<<<
>>>>connected in series are the

0195 preferred in-reactor blending processes. These reactors can be <<<<
>>>>charged with the same catalyst

0196 but operated at different conditions, e.g., different reactant <<<<
>>>>concentrations, temperatures,

0197 pressures, etc, or operated at the same conditions but charged with <<<<
>>>>different catalysts.

0198 +p Examples of processes that can be use to form the blends of this <<<<
>>>>invention include the use

0199 of an ethylene/+60 -olefin polymerization catalyst utilized in <<<<
>>>>combination with at least one

0200 additional homogeneous or heterogeneous polymerization catalyst in <<<<
>>>>the same reactor or in

0201 separate reactors that are connected in series or in parallel to <<<<
>>>>prepare polymer blends having

0202 desirable properties. An example of such a process is disclosed in WO <<<<
>>>>+b 94/00500 +l at page +b 29 +l line

0203 +b 4 +l to page +b 33 +l line +b 17. +l The process uses a continuous<<<<
>>>>ly stirred tank reactor (CSTR) connected in

0204 series or parallel to at least one other CSTR or tank reactor. WO +b <<<<

>>>>93/13143 +1 (at page +b 2 +1 lines +b 19⁺¹⁴~~+1 -+b~~)
0205 31+1) teaches polymerizing monomers in a first reactor using a first <<<<
>>>>CGC having a first reactivity
0206 and polymerizing monomers in a second reactor using a second CGC <<<<
>>>>having a second reactivity
0207 and combining the products from the two reactors. Page +b 3, +1 lines <<<<
>>>>+b 25⁺¹⁴~~+1 -+b~~ 32 +1 of WO +b 93/13143 +1
0208 provides teachings about the use of two CGCs having different <<<<
>>>>reactivities in one reactor. WO
0209 +b 97/36942 +1 (page +b 4 +1 line +b 30 +1 through page +b 6 +1 line <<<<
>>>>+b 7+1) teaches the use of a two-loop reactor system.
0210 The relevant teachings of such applications or their corresponding <<<<
>>>>U.S. patents and allowed
0211 applications are incorporated herein by reference for purposes of <<<<
>>>>U.S. patent practice.

0212 +pg, 11

0213 +p The polydispersity (molecular weight distribution or Mw/Mn or MWD) <<<<
>>>>of the polymer

0214 blend generally ranges from at least about +b 2, +l preferably at <<<<
>>>>least about +b 2.1, +l and especially at least

0215 about +b 2.2 +l to about +b 10, +l preferably about +b 6, +l and <<<<
>>>>especially about +b 4.

0216 +p The polydispersity index is typically measured by gel permeation <<<<
>>>>chromatography (GPC)

0217 on a Waters +b 150+l +20 +0 C. high temperature chromatographic unit <<<<
>>>>equipped with three linear mixed bed

0218 columns (Polymer Laboratories (+b 10 +l micron particle size)) <<<<
>>>>operating at a system temperature of

0219 +b 140+l +20 +0 C. The solvent is +b 1,2,4+l -trichlorobenzene from <<<<
>>>>which about +b 0.5+l % by weight solutions of the

0220 samples are prepared for injection. The flow rate is +b 1.0 +l <<<<
>>>>milliliter/minute, and the injection size is

0221 +b 100 +l microliters.

0222 +p The molecular weight determination is deduced by using narrow <<<<
>>>>molecular weight

0223 distribution polystyrene standards (from Polymer Laboratories) in <<<<
>>>>conjunction with their elution

0224 volumes. The equivalent polyethylene molecular weights are determined <<<<
>>>>by using appropriate

0225 Mark-Houwink coefficients for polyethylene and polystyrene (as <<<<
>>>>described by Williams and

0226 Ward in^{ib} Journal of Polymer Science,^l Polymer Letters, Vol. +b 6, +l <<<<
>>>>(+b 621+l) +b 1968+l) to derive the equation:+ps

0227 +ti M+hd polyethylene+l +32 (+i a+l) (M+hd polystyrene+l)+hu b+ps

0228 +ps In this equation, $a + 32 + b \cdot 0.4316 + 1$ and $b + 32 + b \cdot 1.0 + 1$ Weight <<<<
>>>>average molecular weight, M_w , is calculated in

0229 the usual manner according to the formula: +ps

0230 $+ \sum_i \frac{M_i}{M} w_i + 32 + 93 \left(\frac{w_i}{M} \right) (M_i + 1) + ps$

0231 +ps where w_i and M_i are the weight fraction and <<<<
>>>>molecular weight respectively of the i th fraction

0232 eluting from the GPC column. Generally, the M_w of the polymer blend <<<<
>>>>ranges from about

0233 $+b \cdot 10,000 + 1$ preferably about $+b \cdot 20,000 + 1$ more preferably about $+b$ <<<<
>>>>40,000, $+1$ and especially about $+b \cdot 60,000 + 1$ to

0234 +pg,12

0235 about +b 1,000,000, +l preferably about +b 800,000, +l more <<<<
>>>>preferably about +b 600,000, +l and especially about

0236 +b 500,000.

0237 +p The polymer blends of this invention cover a range of viscosities, <<<<
>>>>depending upon the

0238 molecular weight of the blend and optional post-polymerization <<<<
>>>>rheological modification. In

0239 general, the blend viscosity is characterized by a Mooney viscosity <<<<
>>>>which is measured according

0240 to ASTM D +b 1646+l -+b 89 +l using a shear rheometer at +b 125+l +20 <<<<
>>>>+0 C. The polymer blend Mooney viscosity

0241 generally ranges from a minimum of less than +b 0.01, +l preferably <<<<
>>>>+b 0.1, +l more preferably about +b 1, +l and

0242 especially about +b 15 +l to a maximum of about +b 150, +l preferably <<<<
>>>>about +b 125, +l more preferably about

0243 +b 100, +l and especially about +b 70.

0244 +p The rheological or shear thinning behavior of the ethylene <<<<
>>>>interpolymer is determined by

0245 measuring the ratio of interpolymer viscosity at +b 0.1 +l rad/sec to <<<<
>>>>viscosity at +b 100 +l rad/sec. This ratio

0246 is known as the Rheology Ratio (RR), $V+b 0.1/+l V+b 100$, +l or more <<<<
>>>>simply, +b 0.1/100. +l The RR is an

0247 extension of $I+hd 10+l /I+hd 2 +l$ and as such, in those instances in <<<<
>>>>which the measurement of $I+hd 2 +l$ and $I+hd 10 +l$ are

0248 difficult, e.g., the $I+hd 2 +l$ is less than +b 0.5, +l or the <<<<
>>>>molecular weight of the interpolymer is relatively

0249 high, or the Mooney viscosity of the interpolymer is greater than <<<<
>>>>about +b 35, +l the RR of the

0250 interpolymer can be measured using a parallel plate rheometer.

0251 +p The density of the polymer blends is measured according to ASTM D-
>>>>+b 792, +l and this

0252 density ranges from a minimum of about +b 0.850 +l grams/cubic
>>>>centimeter (g/cm+hu 3+l), preferably about

0253 +b 0.853 +l g/cm+hu 3+l , and especially about +b 0.855 +l g/cm+hu
>>>>3+l , to a maximum of about +b 0.970 +l g/cm+hu 3+l , preferably

0254 about +b 0.940 +l g/cm+hu 3+l , and especially about +b 0.930 +l
>>>>g/cm+hu 3+l . For those polymer blends that are

0255 elastomers, i.e., with a crystallinity less than about +b 45+l %, the
>>>>maximum density is about +b 0.895, +l

0256 preferably about +b 0.885 +l and more preferably +b 0.875, +l g/cm+hu
>>>>3+l .

0257 +pg,13

0258 +p For polymer blends intended for use as elastomers, the crystallinity <<<<
>>>>ty is preferably less than

0259 about +b 40, +l more preferably less than about +b 30, +l percent, <<<<
>>>>preferably in combination with a melting

0260 point of less than about +b 115, +l preferably less than about +b 105, <<<<
>>>> +l C, respectively. Elastomeric

0261 polymer blends with a crystallinity of zero to +b 25 +l percent are <<<<
>>>>even more preferred. The percent

0262 crystallinity is determined by dividing the heat of fusion as <<<<
>>>>determined by differential scanning

0263 calorimetry (DSC) a of polymer blend sample by the total heat of <<<<
>>>>fusion for that polymer blend

0264 sample. The total heat of fusion for high-density homopolymer <<<<
>>>>polyethylene (+b 100+l % crystalline)

0265 is +b 292 +l joule/gram (J/g).

0266 +p One hallmark of this invention is that a desirable property of one <<<<
>>>>component of the blend

0267 can be enhanced without a significant diminution of one or more <<<<
>>>>desirable properties of another

0268 component. For example, certain blends of this invention exhibit an <<<<
>>>>enhanced low temperature

0269 impact property relative to one component of the blend without any <<<<
>>>>significant diminution of the

0270 glass transition temperature (Tg) of the other component of the <<<<
>>>>blend. Other blends of this

0271 invention exhibit the same phenomena (i.e., no significant diminution <<<<
>>>>of Tg) with respect to

0272 pellet flow (i.e., the ability of pellets made from the blend to move <<<<

>>>>pass one another without

0273 sticking or blocking), compression set for a given crystallinity, <<<<
>>>>melt strength and shape retention.

0274 +p Another hallmark of this invention is that these blends exhibit an <<<<
>>>>improved combination

0275 of low temperature, pellet flow, compression set, melt strength <<<<
>>>>and/or shape retention properties

0276 as compared to an ethylene/+60 -olefin polymer blend of similar <<<<
>>>>composition but in which the

0277 ethylene content of each component is substantially the same.

0278 +p The following examples are provided as a further illustration of <<<<
>>>>the invention. Unless

0279 stated to the contrary, all parts and percentages are by weight.

0280 +pg,14

0281 +cl Specific Embodiment

0282 +p Four elastomers were prepared using a dual loop reactor such as <<<<
>>>>that described in WO

0283 +b 98/49212. +l Each elastomers was prepared under the same <<<<
>>>>conditions with the same reactants and

0284 catalyst and to the same total ethylene content (+b 66 +l weight <<<<
>>>>percent based upon the weight of the

0285 polymer component) as the other elastomers. The control elastomer was <<<<
>>>>a blend of two

0286 essentially identical components, i.e., the component made in the <<<<
>>>>first loop reactor was

0287 essentially the same in composition and properties as the component <<<<
>>>>made in the second loop

0288 reactor. The remaining three elastomers, i.e., Elastomers +b 1, 2 +l <<<<
>>>>and +b 3, +l are embodiments of this

0289 invention. Each is essentially the same as the other and the control <<<<
>>>>except that the ethylene

0290 content of the component made in the first loop reactor is different <<<<
>>>>than the ethylene content of

0291 the component made in the second loop reactor. The composition, <<<<
>>>>Mooney viscosity, weight

0292 average molecular weight (Mw), molecular weight distribution (MWD), <<<<
>>>>temperature of

0293 crystallinity (Tc, both onset and peak), and glass transition <<<<
>>>>temperature (Tg) for each elastomer

0294 and two commercially available elastomers (Dutral+198 +0 +b 4038 +l <<<<
>>>>manufactured and sold by Enichem,

0295 and Nordel+198 +0 IP +b 4770 +l manufactured and sold by Dupont Dow <<<<

>>>>Elastomers) are reported in the
0296 following table.

0297 +pg,15

0298 +t,0150

0299 +p As is evident from the data in the above table, Elastomers +b 1, 2 <<<<
>>>>+l and +b 3 +l not only have a

0300 lower Tg than the control elastomer, but also a lower Tg than the two <<<<
>>>>commercially available

0301 elastomers (both of similar composition). Lower Tg usually means <<<<
>>>>better low temperature

0302 flexibility in such products as seals, belts and automotive hoses.

0303 +p The residual crystallinity at elevated temperatures of Elastomers <<<<
>>>>+b 1, 2 +l and +b 3 +l are compared

0304 with the Control Elastomer in FIG. 1. As can be seen from this graph, <<<<
>>>>as the ethylene split

0305 between the elastomer components increases, the so does the residual <<<<
>>>>crystallinity. Usually, the

0306 larger the residual crystallinity at higher temperatures, the better <<<<
>>>>the shape retention of the

0307 elastomer (neat or deployed in its intended end-use).

0308 +p FIG. 2 reports the modulus G+40 0 of the Control Elastomer, <<<<
>>>>Elastomers +b 1, 2 +l and +b 3, +l Nordel

0309 IP +b 4770 +l and Dutral +b 4038. +l Modulus G+b 3+l +40 , or storage <<<<
>>>>modulus, is another measure of the shape

0310 +pg,16

0311 retention of the elastomer. Here too, Elastomers +b 1, 2 +l and +b 3 <<<<
>>>>+l outperform the Control Elastomer

0312 even with a slightly higher overall ethylene content.

0313 +p Finally, Elastomers +b 1 +l and +b 2 +l were compared with the <<<<
>>>>Control Elastomer for pellet flow.

0314 Elastomers +b 1 +l and +b 2 +l demonstrated superior temperature <<<<
>>>>resiliency and lower blocking than the

0315 Control Elastomer.

0316 +p Although the invention has been described in considerable detail <<<<
>>>>through the

0317 specification and examples, one skilled in the art can make many <<<<
>>>>variations and modifications

0318 without departing from the spirit and scope of the invention as <<<<
>>>>described in the following claims.

0319 +pg,17

0320 +cm What is claimed is:

0321 +cm 1. An ethylene/+60 -olefin polymer blend comprising first and <<<<
>>>>second ethylene/+60 -olefin

0322 polymer components in which the ethylene content of the first <<<<
>>>>component differs by at

0323 least about +b 10 +l weight percent from the ethylene content of the <<<<
>>>>second component.

0324 +cm 2. The blend of claim 1 in which the ethylene content of the <<<<
>>>>first component differs

0325 by at least about +b 15 +l weight percent from the ethylene content <<<<
>>>>of the second component.

0326 +cm 3. The blend of claim 1 in which the +60 -olefin in each <<<<
>>>>component contains from +b 3 +l to

0327 about +b 8 +l carbon atoms.

0328 +cm 4. The blend of claim 3 in which the +60 -olefin in each <<<<
>>>>component is propylene.

0329 +cm 5. The blend of claim 4 in which the first and second ethylene/+6<<<<
>>>>0 -olefin polymer

0330 components further comprise a polyene.

0331 +cm 6. The blend of claim 5 in which the polyene is +b 5+l -<<<<
>>>>ethylidene-+b 2+l -norbornene.

0332 +cm 7. The blend of claim 3 in which the +60 -olefin in the first <<<<
>>>>component is propylene

0333 and the +60 -olefin in the second component contains from +b 4 +l to <<<<
>>>>+b 8 +l carbon atoms.

0334 +cm 8. The blend of claim 7 in which at least one of the first and <<<<
>>>>second ethylene/+60 -olefin

0335 polymer components further comprises a polyene.

0336 +cm 9. An ethylene/(+60 -olefin polymer blend comprising first and <<<<
>>>>second ethylene/+60 -olefin
0337 polymer components, the blend prepared by (i) contacting ethylene, an <<<<
>>>>+60 -olefin, an
0338 activated constrained geometry catalyst and, optionally, a polyene, <<<<
>>>>under polymerization
0339 conditions, in a first reactor to produce the first ethylene/+60 -<<<<
>>>>olefin polymer component, (ii)
0340 transferring the first ethylene/+60 -olefin polymer component to a <<<<
>>>>second reactor and in the
0341 presence of the first ethylene/+60 -olefin polymer component, (iii) <<<<
>>>>contacting fresh ethylene, an +60 -olefin,

0342 +pg,18

0343 an activated constrained geometry catalyst and, optionally, a polyene,<<<<
>>>> under

0344 polymerization conditions to produce the second ethylene/+60 -olefin <<<<
>>>>polymer component, the

0345 polymerizations of the first and second reactors conduct in such a <<<<
>>>>manner that the ethylene

0346 content of the first ethylene/+60 -olefin polymer component is at <<<<
>>>>least +b 10 +l weight percent different

0347 than the ethylene content of the second ethylene/+60 -olefin polymer <<<<
>>>>component.

0348 +cm 10. The blend of claim 9 in which the polymerization conducted in <<<<
>>>>each reactor is a

0349 solution phase polymerization.

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